

CHARACTERISATION OF COKE ON DEACTIVATED HYDRODESULFURISATION CATALYSTS AND A NOVEL APPROACH TO CATALYST REGENERATION

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ABSTRACT

The soft (chloroform-extractable) and hard coke fractions from a suite of deactivated Co/Mo hydrodesulfurisation (HDS) catalysts with carbon contents ranging from 5 to 18% have been characterised. The hard coke accounted for between 50 and 70% of the total carbon, but was responsible for much less of a reduction in BET surface area as the carbon content increased. Indeed, significant variations in structure were revealed by solid state ^{13}C NMR with the aromaticity ranging from 0.6 to over 0.9 with increasing carbon content and time on stream. The relatively high aliphatic contents and atomic H/C ratios for the hard cokes obtained at low levels of carbon deposition (5-7%) suggested that much of the carbon should be removed under reductive conditions. Indeed, hydropyrolysis, in which the deactivated catalysts were heated from ambient to 500°C under a hydrogen pressure of 15 MPa, removed over 90% of the carbon and recovered 70% of the BET surface that had been lost.

INTRODUCTION

Deactivation via coke deposition affects all the catalysts used in hydrocarbon conversion processes with the timescale varying from just a few seconds for fluid catalytic cracking (FCC) of heavy petroleum feeds to several months for naphtha reforming and gas oil hydrotreating. For the latter, controlled oxidation is the established means of regeneration to remove coke (see, for example, refs. 1-3 for hydroprocessing catalysts). However, despite the use of slow heating rates and low oxygen environments, some loss of surface area is inevitably encountered for Ni/Mo and Co/Mo γ -alumina-supported hydroprocessing catalysts and other deleterious effects have been observed, including the loss of Ni promoter due to spinel NiAlO_4 formation⁽⁴⁾.

Thus far, non-oxidative treatments in the form of reductive heating⁽⁴⁾ and solvent extraction⁽⁴⁻⁶⁾ have received very little attention because they only remove the adsorbed oil that comprises the soft or soluble portion of the coke. For example, Teixeira daSilva *et al.*⁽⁴⁾ using a nitrogen/hydrogen mixture for reductive heating after acetone extraction reduced the carbon content of a spent catalyst from hydroprocessing shale oil by approximately 35%. Traditionally, the insoluble or hard coke is considered to be highly intractable aromatic in character even for hydrotreating catalysts operating at relatively low temperatures. To investigate whether or not this is the case, the soft (chloroform-extractable) and hard coke fractions have been characterised for a suite of deactivated Co/Mo HDS catalysts with carbon contents ranging from 5 to 18%. The fact that solid state ^{13}C NMR indicated that the hard coke is normally quite aliphatic and contains small aromatic clusters prompted us to use fixed-bed hydropyrolysis for the reductive regeneration of the catalysts where they were heated from ambient to 500°C under a hydrogen pressure of 15 MPa. This technique typically gives rise to conversions of over 90% for sedimentary organic matter, including low-rank coals and petroleum source rocks (type I and II kerogens)⁽⁷⁾. It has been adapted as an analytical procedure for determining the distribution of organic sulfur forms from H_2S evolution profiles^(7,8) and for covalently-bound biomarkers^(7,9,10). Since the temperatures used in hydropyrolysis are potentially lower than in oxidative combustion regeneration, there is the potential that the irreversible loss of surface area can be reduced which offers the possibility of extending catalyst lifetimes and helping to solve the ever-growing disposal problem for spent catalysts.

EXPERIMENTAL

Ten deactivated Co/Mo HDS catalysts, differing in terms of the run time and catalyst bed position, were supplied by BP/Amoco. The carbon contents of the catalysts investigated are listed in Table 1. Samples 1-7 are at different bed heights in the same operation. The final sample (no. 10) with a carbon content of 18% was obtained from a unit that had been left running for 8 years. All the catalysts were extracted in chloroform under reflux to recover the soft coke for

characterisation (designated soft coke I). To isolate the hard coke, one of the low (no. 8) and the high carbon (no. 10) chloroform-extracted catalysts were demineralised using HF/HCl as used previously on FCC catalysts^(11,12). A final wash with dilute nitric acid (2M at 70°C) was required to dissolve the metal sulphides. The hard coke concentrates (carbon contents > 50%) were then extracted in chloroform with the extracts being designated soft coke II.

Carbon, hydrogen and nitrogen contents of the initial deactivated catalysts, the soft coke fractions and the hard coke concentrates were determined using a Perkin-Elmer 2400 analyser and sulphur contents were measured using the Sulphazo III method. BET measurements were carried out using a Micromeritics ASAP 2000 apparatus on the deactivated catalysts before and after chloroform extraction and on two of the hard coke concentrates. A Bruker 250 MHz instrument was used to obtain the ¹H NMR spectra of the soft cokes in chloroform-d. HPLC analysis was carried out using Shandon Scientific Hypersil CTA column in conjunction with a Waters 486 UV detector. The soft cokes were separated into aliphatic, aromatic and polar fractions by open column adsorption chromatography using activated silica gel. Size exclusion chromatography (SEC) was carried out to estimate the number and weight average molecular masses (M_n and M_w) of the soft cokes based on polystyrene standards, a mixed bed PL gel column being employed with RI detection and chloroform as the eluting solvent.

The solid state ¹³C NMR measurements on the hard coke concentrates were carried out at 25 MHz on a Bruker MSL 100 spectrometer with MAS at 4.5-5.0 kHz to give spectra in which the sideband intensities are only ca. 6-7% of the central aromatic bands. A contact time of 1 ms was used for the cross polarisation (CP) measurements and the ¹H decoupling and spin-lock field was ca. 60 kHz. The FIDs were processed using a Lorentzian line broadening factor of 50 Hz. To determine the fraction of protonated and non-protonated carbon, four delay periods between 1 and 100 μ s were employed in dipolar dephasing experiments.

Fixed-bed hydrolysis tests at 15 MPa were conducted using either ca. 0.5 or 1 g of sample for the low and high carbon deactivated catalysts selected for detailed investigation. For some tests, the deactivated catalysts (extrudates) were ground and diluted in sand. The procedure used has been described elsewhere^(7,9,10), a slow heating rate of 5°C min⁻¹ being used to maximise conversion.

RESULTS AND DISCUSSION

Characteristics of the soft coke

The soft coke obtained from the as-received catalysts accounts for between 25 and 50% of the total carbon with the mean being close to 35% (Table 1). Thus, the high carbon in the case of sample no. 10 does not markedly affect the distribution of soft to hard coke. After demineralisation, further extract was obtained (soft coke II) but the yield was typically no more than ca. 3% of the total carbon. Table 2 summarises the analytical data obtained for the chloroform extracts obtained from both the as-received catalysts (soft coke I) and after the demineralisation treatment (soft coke). Overall, the H/C ratios, heteroatom contents, molecular masses and compound class distributions indicate that the easily extractable soft coke can be described as "heavy and generally polar gas oil" (Table 2). The gas chromatographic profiles comprised broad unresolved shoulders containing small peaks from *n*-alkanes. ¹H NMR indicated that the soft cokes have low aromaticities (6-8 mole % aromatic hydrogen) consistent with their relatively high aromatic H/C ratios (Table 2). Both HPLC and ¹H NMR indicated that the average ring size is quite small (1-2 rings as for initial gas oil).

The relatively small quantities of soft coke physically entrapped within the pore structure that were amenable to extraction after demineralisation (soft coke II) have considerably higher molecular masses, lower atomic H/C ratios and higher heteroatom contents than their easily extractable counterparts (Table 2). If the adsorbed soft coke is the major precursor of hard coke, then it is a case of concentrating the polars as opposed to the large polycyclic aromatic hydrocarbon moieties from the initial gas oil. Further, the aliphatic nature of the soft coke indicates that considerable condensation is required to form large aromatic structures.

Characteristics of the hard coke

The CP/MAS ¹³C NMR spectra of the hard coke concentrates from the low and high carbon catalysts (nos. 8 and 10, respectively) are shown in Figure 3. The aromaticities and the average ring sizes derived from the normal and dipolar dephasing ¹³C NMR spectra are listed in Table 3. There is a remarkable difference between the two samples. The concentrate from the low carbon catalyst is quite aliphatic in character (aromaticity of ca. 0.6) and contains relatively small aromatic clusters. In contrast, the hard coke from the high carbon catalyst has a high aromaticity and contains large clusters (Table 3). In fact, it is quite comparable in bulk structural terms to catalytic coke obtained in FCC^(11,12). These results indicate that aromatisation to large cluster sizes proceeds extremely slowly under hydrotreating conditions (relatively low temperature, high hydrogen pressure). Further, the aliphatic nature and small aromatic ring

cluster size for the hard coke obtained under typical operating conditions suggests that it should readily be converted into oil by hydrolysis under the conditions where high conversions are achieved for type I and II kerogens and low-rank coals⁽⁷⁾.

Reductive regeneration using hydrolysis

Figure 2 compares the carbon contents of the received, the chloroform-extracted and the hydrolysed samples for the low and high carbon samples. Carbon conversions of over 90% were achieved for the low carbon catalyst consistent with the bulk structural characteristics of the hard coke concentrate (Table 3). In contrast for the high carbon sample, hydrolysis removed only ca. 60% of the carbon which corresponds to ca.40% of the hard coke (Figure 2). Neither sample size nor grinding and diluting the samples in sand had a significant effect on the levels of carbon removal, the differences being below 5% of the total carbon.

Figure 3 indicates that the surface area recovery for the low carbon sample (ca. 70%) is comparable to that achieved by controlled combustion. In contrast, for the high carbon sample, the surface area recovery is considerably less than that by combustion (by ca. 30 m² g⁻¹) due to the low carbon conversion. For this catalyst, extraction of the soft coke alone gives rise to approximately 70% of the surface area recovery compared to controlled combustion (Figure 3). Thus, the soft coke is proportionally responsible for a much greater loss of surface area than in the case of the low carbon catalyst.

It is probable that a combination of a lower temperatures (450°C) and higher pressures to those employed in this initial study should probably represent the optimum conditions for maintaining catalyst surface area. It was observed that hydrolysis gave rise to sulfur reductions of up to 2% w/w. In order to prevent reduction of the promoter to the corresponding metal (Ni/Co), hydrolysis should be carried out in the presence of a small amount of hydrogen sulphide to help maintain the catalyst to remain in a reasonably fully sulfided form. Hydrolysis for virtual complete carbon removal will need to be carried out off-line since the combination of temperature, pressure and flow rate required cannot be achieved in hydrotreating units. In terms of potential applications, carbon-supported catalysts may represent the major area since these cannot be regenerated oxidatively.

CONCLUSIONS

Soft coke accounts for typically about one-third of the carbon on deactivated catalysts from gas oil hydrotreating units. The soft coke is highly polar in nature, but possesses significant aliphatic character. The hard coke obtained in normal operating situations (5-7 % carbon) has a carbon aromaticity of not much more than 50% and comprises small clusters. However, prolonged usage (carbon content > 15%) leads to a vast increase in aromaticity (>0.90) and ring cluster size. The majority of the hard coke obtained under normal operating conditions (> 80%) can be effectively removed by carrying out fixed-bed hydrolysis at 15 MPa and 500°C. This gives rise to a recovery in surface area comparable to that achieved oxidatively. Further improvements in hydrolysis in terms of surface area recovery are likely by operating at lower temperatures and higher pressures.

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REFERENCES

1. Arteaga, A.; Fierro, J.L.G.; Dellanay, F.; Delmon, B. *Appl. Catal.* **1986**, *26*, 227.
2. George, Z.M.; Mohamed, P.E.; Tower, R. *Proc. Int. Congr. Catal.*, **9th 1988**, 230.
3. Teixeira da Silva, V.L.S.; Frety, R.; Schmal, M. *Ind. Chem. Eng. Res.* **1994**, *33*, 1692.
4. Teixeira da Silva, V.L.S.; Lima, F.P.; Dieguez, L.C.; Schmal, M. *Ind. Eng. Chem. Res.* **1998**, *37*, 882.
5. Maraf, M.; Stanislaus, A. *Appl. Catal.* **1989**, *47*, 85.
6. Babcock, K.E.; Hiltzik, L.; Ernst, W.R.; Garruthers, J.D. *Appl. Catal.*, **1989**, *61*, 295.
7. Rocha, J.D.; Brown, S.D.; Love, G.D.; Snape, C.E. *Journal of Anal. and Appl. Pyrolysis* **1997**, *40-41*, 91.
8. Brown, S.D.; Sirkecioglu, O.; Snape, C.E.; Eglinton, T.I. *Energy & Fuels* **1997**, *11*, 532.
9. Snape, C.E.; Love, G.D.; Murray, I.P.; Bailey, N.J.L. *Organic Geochem.* **1998**, *29*, 1487.
10. Love, G.D.; McAulay, A.D.; Snape, C.E.; Bishop, A.N. *Energy & Fuels* **1997**, *11*, 522.

11. Snape, C.E.; McGhee, B.J.; Andr sen, J.M.; Hughes, R.; Koon, C.L.; Hutchings, G.
12. Snape, C.E.; McGhee, B.J.; Martin, S.C.; Andr sen, J.M. *Catalysis Today* 1997, 37(3), 285.

Table 1 Coke contents for the suite of deactivated HDS catalysts

Sample no.	%C	%Soft coke 1 (carbon basis)
1	5.6	30
2	6.1	25
3	5.3	33
4	6.5	36
5	6.4	28
6	6.5	39
7	7.4	32
8* (3 months)	8.2	49
9	6.8	43
10* (8 years)	17.8	31

Samples 1-7 from the same unit, 1 at top and 7 nearest bottom of bed.

* selected for detailed characterisation.

Table 2 Summary of the soft coke composition for the suite of deactivated HDS catalysts

	Soft Coke I	Soft Coke II
Atomic H/C	1.60 - 1.85	1.5
% N	0.5-0.8	1.3
% S	< 0.2	< 0.2
%O (by difference)	3-6	>10
% Aliphatics	<10	n.d.
% Aromatics:	<20	n.d.
% Polars:	>70	n.d.
M _n :	200-300	240-340
M _w :	270-380	420-460

n.d. = not determined.

Table 3 Summary of structural parameters for the hard coke concentrates

Parameter	Low carbon (no. 8)	High carbon (no.10)
Carbon aromaticity	0.58	0.42
Fraction of aromatic C that is non-protonated	0.56	0.53
Fraction of aromatic C that is bridgehead	0.1-0.2	0.44
Inferred ring size	1-2	8

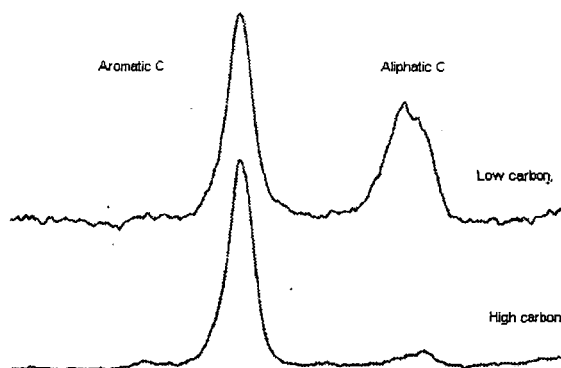


Figure 1. Solid state CP/MAS ¹³C NMR spectra of hard coke concentrates from low carbon (top) and high carbon (bottom) deactivated HDS catalysts.

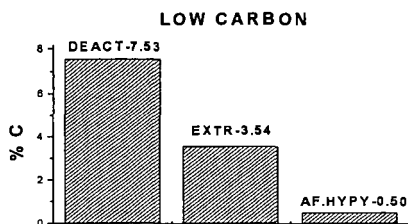
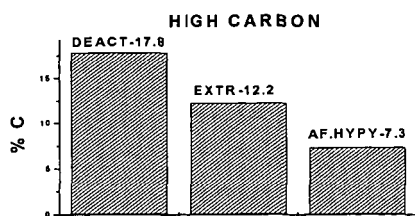


Figure 2. Carbon contents for the low and high carbon deactivated HDS catalysts – as received, after chloroform extraction and after hydropyrolysis.

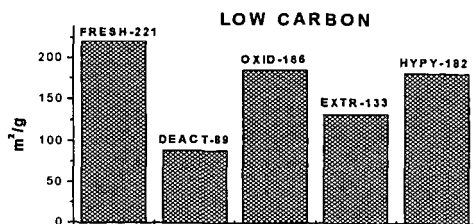
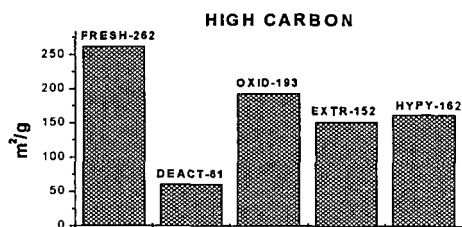


Figure 3. BET surface areas for the low and high carbon deactivated HDS catalysts – as received, after chloroform extraction and after hydropyrolysis.